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The transport of solvents and other small molecules in polymer solutions is important in many areas such as reaction rates, drying of coatings, plasticizer loss, curing of resins, elimination of residual monomer, and controlled drug release. Some of the work done in our laboratory on the diffusion of small molecules in polymer solutions and dispersions is reviewed. The diffusion data was used to test the Vrentas and Duda's free-volume theory for self-diffusion coefficients; test the independence of the normalized solvent self-diffusion for several polymer-solvent systems; and predict the solvent loss curves for drying of coatings based on solvent self-diffusion coefficients.

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by

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NMR Measurements of Solvent Self-Diffusion Coefficients in Polymer Solutions

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INTRODUCTION

The transport of solvents and other small molecules in polymer solutions is important for a variety of reasons. For example, small molecule transport in polymer solutions may control the rate of chemical reactions, the drying of coatings, the loss of plasticizer, curing of resins, elimination of residual monomer, and controlled release of drugs. The role of diffusion in different chemical systems has been reviewed(1,2) along with the measurement of diffusion coefficients in general(3-4).

In this paper we review some of the work which has been done in our laboratory on the diffusion of small molecules in polymer solutions and dispersions. The measured diffusion coefficients are shown to be useful for scientific studies as well as being predictive tools for industrial processes. For reference a number of reviews have been written on the technical aspects and applications of the technique (5-9). Some of these(5,7,8) have sections dealing with polymer systems.

PULSED-GRADIENT SPIN-ECHO NMR

The potential use of NMR to measure self-diffusion coefficients was recognized as early as the 1950's. The basis of the technique is that the nuclear spins are tagged via their precessional frequencies. The precessional frequency of a nuclear spin, ω, is given by:

$$\omega = -\gamma H(x) \tag{1}$$

where γ is the magnetogyric ratio of the nucleus and H is the magnetic field strength which can be made to vary as a function of position, x. Normally, the magnetic field is uniform (homogeneous) over the sample volume so that all nuclei of the same type have the same resonance (precessional) frequency. If a magnetic field gradient is used (i.e. H varies with position), the precessional frequencies will vary with position and consequently the nuclear spins will be "tagged" by their position.

The basic technique currently used by most researchers is the pulsed-gradient spin-echo (PGSE) method based on the work of Stejskal and Tanner (10) as modified by Stilbs and Moseley(11). The pulse sequence is shown in Figure 1. It consists of a normal spin-echo pulse sequence with two magnetic gradient pulses added. During the spin echo (90°-Δ-180°-Δ-echo) sequence, normal spin-spin relaxation, T_2, occurs during the time 2Δ after which the echo is formed. A series of spectra are then collected as a function of the duration of the magnetic field gradient
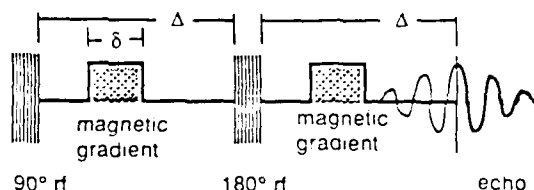

Figure 1. The PGSE pulse sequence

pulse, δ. The resulting intensity can then be represented by:

$$I = I_0 \exp(-2\Delta/T_2) \exp(-\gamma^2 G^2 \delta^2(\Delta-\delta/3)) \tag{2}$$

where G is the magnetic gradient field strength and D is the self-diffusion

coefficient. Other complicating terms have been omitted. Typical G values used range from 1 to 100 gauss/cm. It is important to note that if the experiments are done at fixed Δ that the diffusion coefficient can be probed independently of T_2, however the value of T_2 still has an important effect in the attenuation of all of the spectra. In practical terms this means that as the diffusion coefficient gets slower (this usually corresponds to smaller T_2), larger gradients are needed to measure self-diffusion coefficients.

SOLVENT DIFFUSION AND FREE VOLUME

Shown in Figure 2 is an example of the results of PGSE experiments on toluene in polystyrene solutions(12) as a function of temperature. These results show that the solvent self-diffusion coefficient varies over two orders of magnitude from 0 to 90% polymer. These measurements were made on JEOL FX-90 and FX-100 instruments with field gradients of about 5 G/cm. To obtain self-diffusion coefficients at higher concentrations of polymer a larger gradient is needed such as that used by von Meerwall (5,7). These data are adequately described by the free-volume based theory of Vrentas and Duda (13) using their correlative approach which requires that two parameters to be fitted to the experimental data.
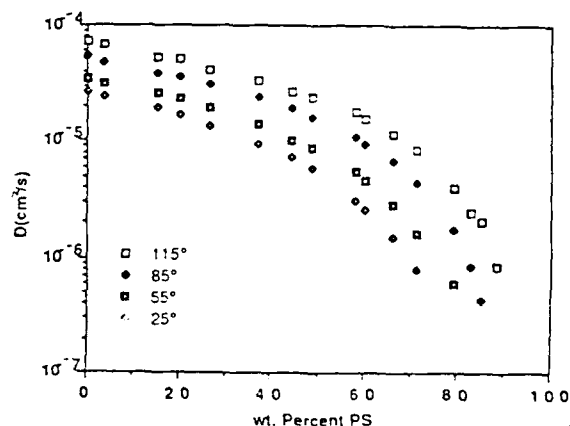

Figure 2. Self-diffusion coefficients of toluene in polystyrene solutions(12).

A free volume approach has also been used to compare solvent self-diffusion data with NMR relaxation data in the poly(isopropyl acrylate)-d/ chloroform system(14). The relaxation time measurements were the T_2's of the backbone deuterons. For this system it was found that both concentration and temperature superpositions for both sets of data were identical (within experimental error) suggesting that both types of phenomena were sensitive to the same free volume fraction. This type of analysis needs to be performed on other types of polymer systems.

In the dilute and semi-dilute regimes, it has been noted that the normalized solvent self-diffusion coefficients in polymer solutions could be superimposed at lower concentrations. Shown in Figure 3 are the toluene self-diffusion coefficients normalized by the self-diffusion coefficient of the pure solvent at various temperatures. It is obvious that the differences between the different temperature data are small at low concentration and become larger as the concentration increases. This effect has been verified by NMR for polystyrene in either toluene or cyclohexane, poly(ethylene oxide) in water(15), and also by forced Rayleigh scattering of poly(vinyl acetate) in methyl red/toluene solutions(16). The normalized data all fall on the same plot regardless of the strength of the interaction between the polymer and the solvent for binary systems. This type of analysis may not hold in some three component systems where one small molecule is preferentially attracted to the polymer(16).
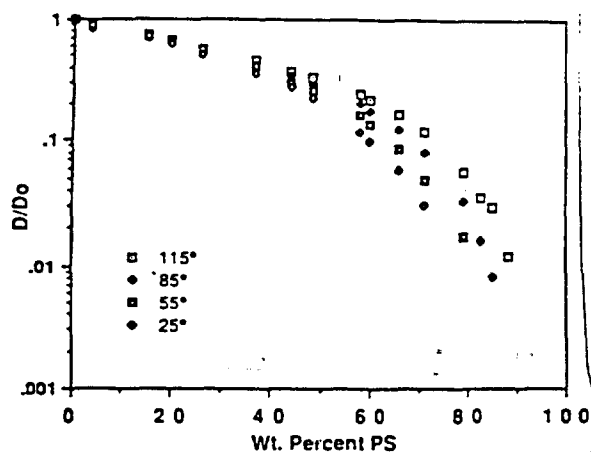
Figure 3. Normalized self-diffusion coefficients of toluene in polystyrene solutions.

There are a variety of mechanisms which can be used to rationalize the apparent superposition of diffusion coefficients including obstruction(12) and also free volume effects(17). Regardless of the cause of this phenomena, it can still be used for its predictive nature. An example, of this was demonstrated in the diffusion of toluene in swollen polystyrene beads(18). In this system it was found that the self-diffusion coefficients of the solvent within the beads could be predicted on the basis of the solution diffusion coefficients plus knowledge of the solvent uptake from the swelling ratio. In this case the actual measurement of the diffusion coefficient is complicated because contributions from the solvent inside and outside the beads, plus exchange, must be considered.

SOLVENT DIFFUSION AND DRYING OF COATINGS

Solvent self-diffusion coefficients have been shown to be useful for prediction of physical phenomena such as the drying of coatings. Solvent loss curves for coatings systems usually show behavior which can be divided into loss controlled by volatility, at early times, and evaporation, at later times(19). In the diffusion controlled region, the mutual diffusion coefficient of the system should control the transport of solvent to the surface of the coating. The NMR experiment provides a measurement of the self-diffusion coefficient. Fortunately, in the regime of interest (high solids contents) the two measurements approach each other, being identical in the limit of zero solvent content. An example of a comparison of data for the toluene-polystyrene system at 110 °C is shown in Figure 4. The self-diffusion coefficients were interpolated from data at temperatures higher and lower than 110 °C and the mutual diffusion data was from the literature(20). As can be seen from the figure, the two sets do approach each other at high concentrations of polymer.
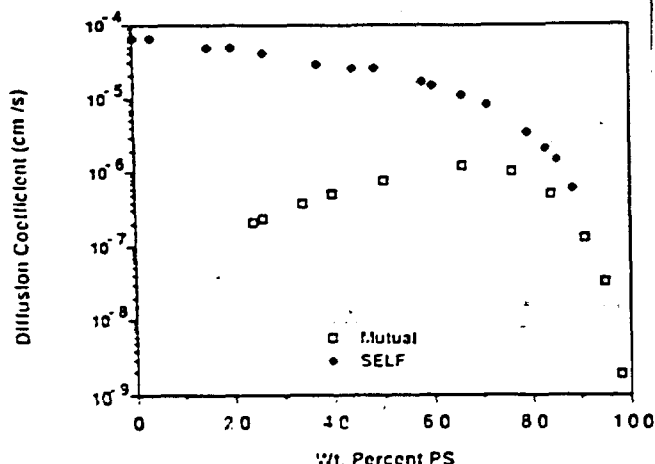

Figure 4. Mutual(20) and self toluene diffusion coefficients for the polystyrene-toluene system at 110 C

Shown in Figure 5 are the curves for the loss of toluene as a function of time along with our predictions(21). To simulate the drying curves a finite difference model was used(21) along with the evaporation rate of pure toluene, the Flory-Huggins interaction parameter, and solvent self-diffusion coefficient data(12). The solvent self-diffusion data were extrapolated and interpolated with the use of the Vrentas-Duda theory(13). As can be seen in the figure, the agreement between the experimental and predicted diffusion curves is excellent, particularly considering that no adjustable parameters were used.
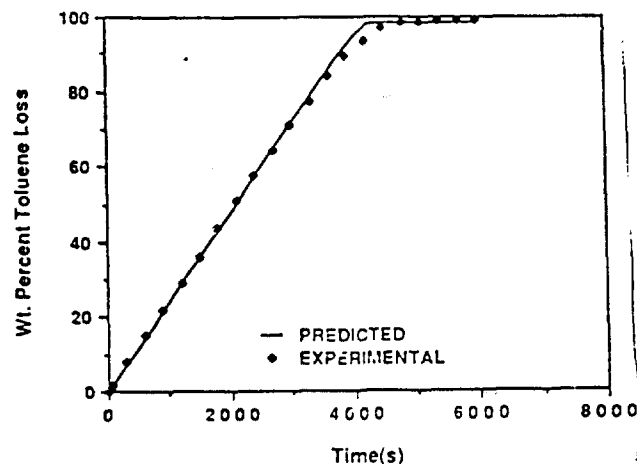

Figure 5 Predicted and experimental drying curves for polystyrene at 25°C.

CONCLUSIONS

The NMR technique for measuring self-diffusion coefficients has been applied to a variety of solvent-polymer systems. There are a variety of important problems which can be solved or understood using this type of data. In the future, more and further-reaching applications are expected.

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